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(71) Applicant : **ATOHAAS HOLDING C.V.
Schipholpoort 60
NL-2034 MB Haarlem (NL)**

(72) Inventor : **Rigamonti, Marco
Via Pastrengo 17
Milano (IT)**

(74) Representative : **Sama, Daniele
Sama Patents
Via Masera, 10
I-20129 Milano (IT)**

(54) **Process for the preparation of antiscratch and antiabrasion shaped articles based on acrylic polymers.**

(57) The invention refers to a process to render antiscratch and antiabrasion shaped articles based on thermoplastic acrylic polymers consisting in coating the article by a composition comprising

a) 40-98.5% by weight of at least a (meth)acrylic monomer and/or oligomer having at least two polymerizable double bonds ;

b) 1-20% by weight of at least a (meth)acrylic monomer and/or oligomer containing polar groups ;

c) 0.5-10% by weight of a UV photoinitiator ; optionally colloidal silica, UV stabilizers and non ionic surfactants and by polymerizing and crosslinking in situ said composition by UV light, at temperatures of 20-65°C.

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The present invention relates to a process to render antiscratch and abrasion-resistant the surface of shaped articles, plates and films based on thermoplastic acrylic polymers by coating with a mixture of particular polymerizable acrylic monomers and UV photoinitiators and subsequent polymerization and crosslinking by UV radiation of the coating.

The invention relates, moreover, to antiscratch and abrasion-resistant shaped articles obtained by the aforesaid process.

It is known that one of the problems met in the use of plates and films, in particular the transparent ones, based on thermoplastic acrylic polymers, such as, for instance polymethylmethacrylate (PMMA), is due to their easy scratching and abrasion with consequent decrease of their transparence and decay of the surface aspect.

The art has suggested various surface treatments of plates and shaped articles of thermoplastic polymers, among which acrylic polymers, in order to avoid the aforesaid inconvenience.

Such treatments generally comprise the application on the article or on the thermoplastic plate (substrate) of a layer of polymerizable unsaturated monomers, which was polymerized and crosslinked in situ by heating at high temperatures, from 80°C to the Tg of the substrate, in the presence of radical polymerization initiators.

A polymerized and crosslinked coating of sufficient hardness improving the abrasion resistance of the thermoplastic article was obtained in this way.

However such treatments were not free from inconveniences, as they had to be carried out in oxygen-free place, in particular in an inert atmosphere (nitrogen) in order to avoid inhibition due to oxygen on the polymerization and crosslinking carried out at high temperatures and degradation of the polymeric substrate with formation, besides, of undesired yellowish coloring. Moreover, the so obtained coatings did not always show a good adhesion to substrate and a good transparence.

It resulted therefore difficult and complex to carry out said treatments in absence of oxygen, in particular in industrial plants for the continuous manufacture of plates and films of thermoplastic polymers.

There were moreover suggested treatments wherein the monomeric layer applied on the polymeric substrate was polymerized and crosslinked by using UV rays in the presence of photoinitiators, which

higher than 40°C, such as not to affect the dimensional stability of the polymeric substrate, as well its mechanical, aspect and transparence properties, or, anyway, to avoid degradation thereof.

However the polymerized and crosslinked coatings so obtained showed an insufficient or poor adhesion to the polymeric substrate.

In order to obviate the insufficient adhesion to the substrate of the polymerized and crosslinked coating it was suggested in patent DE 2,928,512 to carry out polymerization and crosslinking by UV of the monomeric layer at high temperatures from 70°C to 150°C, at any rate near the Tg of the polymer forming the substrate, using monomers with at least two double bonds, having a boiling temperature higher than that at which polymerization and crosslinking are carried out.

In the case of thermoplastic substrates based on polymethylacrylate (PMMA), the advantageous temperatures to obtain a good adhesion were from 90°C to 110°C.

The method suggested in the aforesaid German patent, wherein it results necessary to operate at high temperatures, near the Tg of the acrylic polymer, for obtaining good adhesions, leads however to a worsening of the mechanical properties of the acrylic substrate, to the formation of surface defects, to its brittleness and to the degradation of its surface by formation of undesired yellowish or orange coloring and to a reduction of its transparence.

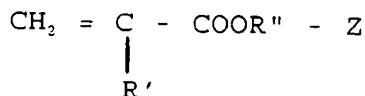
It has now been found a simple process to render antiscratch and abrasion-resistant shaped articles based on thermoplastic acrylic polymers, in particular PMMA, which does not show the drawbacks shown by the known processes, consisting in coating the surface of the articles with a mixture which comprises acrylic monomers having at least two polymerizable double bonds and acrylic monomers having polar groups and an UV photoinitiator, and in polymerizing and crosslinking at UV light said mixture at low temperatures from 20°C to 65°C.

The articles obtained by said process show a good surface hardness, high antiscratch and abrasion resistance properties, with an optimal adhesion to the substrate of the polymerized and crosslinked monomeric coating; moreover they maintain unchanged their transparence and their mechanical and surface aspect properties without showing undesired yellowish coloring.

Object of the present invention is therefore a process for preparing shaped articles, plates and films based on acrylic thermoplastic polymers, having antiscratch properties and abrasion-resistant, consisting in applying on the surface of a shaped article based on thermoplastic acrylic polymers an homogeneous layer of a monomeric composition com-

(meth)acrylic monomer and/or oligomer having at least two polymerizable double bonds and a boiling temperature higher than the Tg of the acrylic polymers forming the article

b) from 1 to 20% by weight of at least a polar (meth)acrylic monomer having the following formula



wherein:

R' is H, CH₃; R'' is alkylene C₂-C₆; Z is -OH, -COOH, -SO₃H, -NH₂, -CONH₂ and/or of its oligomers formed by 2 to 7 monomeric units

c) from 0.5 to 10% by weight of a polymerization initiator at UV light

d) from 0 to 3% by weight of colloidal silica and/or colloidal metal oxides

e) from 0 to 8% by weight of UV stabilizers

f) from 0 to 3% by weight of non ionic surfactants, the sum of the amounts a+b+c+d+e+f being 100, and in submitting the article so coated to UV radiation at temperatures from 20° to 65°C.

As thermoplastic polymers forming the shaped article one can cite for instance (co)polymers, generally transparent, of esters of the (meth)acrylic acid, in particular PMMA, transparent alloys of said (co)polymers with polyvinylchloride (PVC) or polyvinylidene-fluoride (PVDF), polymethylmethacrylate containing in dispersed phase acrylic elastomers (shock resistant PMMA).

Polyfunctional (meth)acrylates, for instance of glycols, polyols, ethoxylated polyols, aliphatic urethanes, melamine and their blends can be utilized as components (a).

Examples of such compounds are tripropylene glycol diacrylate (TPDGA), 1,6-hexandiol triacrylate (HDDA), trimethylolpropane triacrylate (TMPTA), pentaerythrit triacrylate (PETIA), triacrylates of ethoxylated trimethylolpropane, poly(meth)acrylate urethanes obtained by reacting polyols with isocyanates and hydroxyethyl(meth)acrylates, unsaturated diacrylmelamine.

The aliphatic hexacrylate urethane and the unsaturated diacrylmelamine and their mixtures with TPGDA, HDDA, TMPTA, PETIA have proved to be particularly suitable.

Hydroxyalkyl(meth)acrylates, carboxyalkyl(meth)acrylates, sulfoalkyl(meth)acrylates, aminoalkyl(meth)acrylates, aminocarbonylalkyl(meth)acrylates can be used for instance as components (b).

Hydroxyalkyl(meth)acrylates, in particular the hydroxyethylmethacrylate (HEMA) and carboxyalkyl(meth)acrylates, in particular carboxyethylacrylate (βCEA) have proved to be particularly suitable.

As components (c) can be used radical polymerization initiators at UV light known in the art, such as for instance 2-hydroxy-2-methyl-1-phenyl-propan-1-one- (DAROCURE-1173^(R) of Ciba-Geigy), 1-hydroxy-cyclohexyl-phenyl-ketone (IRGACURE-184^(R) of Ciba-Geigy) and those based on benzophenone such as for instance ESACURE KIP 100 E^(R) of Fratelli

Lamberti, or their mixtures.

Component (d) is generally used in small amounts, preferably of 0.1-1% by weight, as viscosity regulator of the coating monomeric mixture; to this purpose colloidal silica having a diameter of the primary particles lower than 20 nanometers and a pH of 3-4, have resulted particularly suitable.

As component (e), the UV stabilizers known in the art can be used in order to protect the polymeric article during crosslinking of the coating via UV.

They are generally consisting of benzotriazols and by sterically hindered amines, such as for instance TINUVIN 1130^(R) and TINUVIN 2292^(R) of Ciba-Geigy.

Component (f) is generally used in small amounts as fluidifying agent, especially if the mixture a+b+c results of little fluidity, in order to eliminate the spreading defects of such mixture and so improve the coating aesthetic aspect.

Fluoroaliphatic polymeric esters, such as FC-430^(R) of 3-M are particularly suitable to this purpose.

The coating monomeric composition, its viscosity being adjustable at will by varying the monomers percentage, use of colloidal silica and/or of fluidifying non ionic surfactants, can be applied on the substrate with anyone of the methods known in the art, for instance by spraying, spreading, so as to form an homogeneous coating layer capable of forming, after polymerization and UV crosslinking, a film having a 0.5-40 μm thickness, preferably from 5 μm to 15 μm.

Films having high thicknesses generally result more rigid and less flexible.

The temperatures at which polymerization and crosslinking of the coating monomeric layer a+b+c are carried out can vary from 20° to 65°C, preferably from 20° to 60°C, more preferably from 30 to 55°C.

It is generally not necessary to operate in absence of oxygen, however if relatively long times of UV radiation are to be used, it is advisable to operate under nitrogen flow to avoid a certain inhibition due to oxygen.

The process according to the present invention can be carried out continuously, integrated with the preparation, for instance by filming and extrusion, of the support shaped article.

More particularly the present process can be continuously carried out, on a line of extrusion of acrylic plates in areas wherein the temperature of the plate is lower than 65°C.

In order to avoid overheating of the plate, due to the infrared component of the UV radiation emitted from UV lamps commonly used for polymerizing and crosslinking the coating, one can utilize UV lamps having a reduced infrared emission or placing between the UV lamp and the plate a filter eliminating most of infrared radiations, such as for instance a PYREX^(R) of a 2-3 mm thickness and/or utilize a flow of cold gas (air and/or nitrogen) to maintain the sys-

tem within the temperature limits indicated above.

A further object of the present invention are shaped articles, plates and films based on thermoplastic acrylic polymers having an antiscratch and abrasion-resistant coating, obtained by the process of the present invention.

The shaped articles coated according to the process of the present invention show high antiscratch and abrasion resistance properties, an optimal adhesion of the coating film to the acrylic substrate, maintain unchanged their original transparence, their dimensional stability, their mechanical characteristics and do not show undesired yellowish coloring.

In order to verify the effectiveness of both antiscratch and antiabrasion treatment, two distinct methods have been used, since the two properties are distinguishable.

To measure the scratch resistance, the hardness test has been used with wood pencils according to ASTM D 3363.

To measure the abrasion resistance it has been adopted the method by falling of powder of silicon carbon on the treated plate and the consequent loss of transparence has been measured according to ASTM D 673.

The adhesion of the film to the support was determined by applying on the film an adhesive tape type 610 (3 M) according to ASTM 3359 standard.

Optical tests have been carried out to verify the effectiveness of the antiabrasion paints.

The transmittance and turbidity to light tests have been carried out according to ASTM D 1003.

The yellow index has been determined according to ASTM D 1925.

Some examples are given for illustrative purposes.

EXAMPLE 1

A PMMA plate of a 3 mm thickness was coated by spreading with a layer of 10 μ m of a mixture containing 50% by weight of aliphatic hexacrylate urethane (EB 1290, UCB), 40% of 1,6 hexandiol diacrylate (HDDA), 8% of hydroxyethylmethacrylate (HEMA) and 2% of UV photoinitiator (DAROCURE 1173^(R), Ciba-Geigy).

The formulation was polymerized with two 80 W/cm UV lamps with dichroic quartz, at a feeding rate of 1 m/min.

the PMMA plate, a pencil resistance of 6 H hardness (hardness from B to H for untreated PMMA), an haze after the falling of two thousand grams of silicon carbide of about 6% (untreated PPMA plate about 11.5%) and an unchanged yellow index (plate + film).

EXAMPLE 2

A HIPMMA plate (shock resistant polymethylmethacrylate; matrix = PMMA, dispersed phase = acrylic elastomers and PMMA) of a 3 mm thickness was coated by spreading with a 10 μ m layer of a mixture similar to that of example 1, but with the following differences:

use of 6% by weight of hydroxyethylmethacrylate (HEMA) and of 4% of UV photoinitiator (DAROCURE 1173^(R), 1% by weight of TINUVIN 2292^(R) and 1% of TINUVIN 1130^(R) (stabilizers at UV, Ciba-Geigy) were added to 100% of the mixture.

The crosslinking conditions are the same as in example 1. The crosslinked film showed an optimal adhesion on the HIPMMA plate, a pencil resistance of 5 H hardness (untreated HIPMMA hardness = 2B), an haze after the falling of two thousand grams of silicon carbide of about 7% (untreated HIPMMA plate = 18.5%) and an unchanged yellow index. The film shows moreover a good elasticity.

EXAMPLE 3

A PMMA plate of a 3 mm thickness was coated by spreading with a layer of 5 μ m of a mixture containing 45% of Santolink AM 1290 of Monsanto (62-68% by weight of unsaturated diacrylmelamine as oligomeric phase and 32-28% tripropylenglycoldiacrylate as monomeric phase), 45% of trimethylolpropane triacrylate (TMPTA), 8% of β CEA (carboxy ethyl acrylate, UCB) and 2% of UV photoinitiator (IRGACURE 184^(R), Ciba-Geigy).

HPK Philips lamps were applied (about 25 W/cm), keeping the plate at 10 cm from the lamps and in nitrogen flow at room temperature for a period of 5 minutes.

The treated plate shows good adhesion, a pencil resistance of 7 H hardness (untreated PMMA hardness: from B to H), and an haze after the falling of 2000 grams of silicon carbide of 8% (11.5% plate in untreated PPMA). The yellow index remained unchanged.

EXAMPLE 4

A PMMA plate having a 3 mm thickness was coated by spreading with a 5 μ m layer of a mixture similar to that of example 3.

The crosslinking conditions of example 1 were

The crosslinked film showed the same properties of example 3.

EXAMPLE 5

A PMMA plate of a 3 mm thickness was coated by spreading with a layer of 5 μ m of a mixture containing

50% of TMPTA, 40% of ethoxylated trimethylol propane triacrylate (SR 454, Cray Valley), 5% of pentaerythrite triacrylate (PETIA), 2% of β CEA and 3% of UV photoinitiator (Esacure KIP 100, Fratelli Lamberti). 1% of colloidal silica HDK T30 (Wacker) was added to 100% by weight of the mixture. The crosslinking conditions are the same as in example 1. The cross-linked film showed optimal adhesion on the PMMA plate, a pencil resistance of 5-6 H hardness and an haze after the falling of 2000 grams of silicon carbide of about 5.5 (untreated PMMA plate 11.5%). The plate yellow index has remained unchanged.

EXAMPLE 1 (comparative)

A PMMA plate of a 3 mm thickness was coated by spreading with a 10 μ m layer of the monomeric mixture used in example 1 of DOS 2,928,512, containing 75% by weight of trimethylolpropane triacrylate (TMPTA) 20% by weight of pentaerythrite tetracrylate (PETIA) and 5% by weight of benzoinisobutylether as UV photoinitiator.

Such formulation was polymerized by adopting a 120 W/cm with mean pressure of mercury vapours at the feeding rate of 1 m/min.

The substrate reached a temperature of 95°C.

In these conditions the plate showed a 100% adhesion, an optimal scratch resistance (pencil test = 7H), a fairly good abrasion resistance with an haze after 2000 g SiC = 7.5 (11.5 = untreated PMMA), but a remarkable yellowing.

A certain deformation of the plate and a decay of its mechanical properties, such as for instance the shock and bending resistance were furthermore noticed.

EXAMPLE 2 (comparative)

A PMMA plate of a 3 mm thickness was coated by spreading with a 5 μ m layer of a mixture having the formulation of example 3.

Such formulation was polymerized in air with normal 120 W/cm lamps having a mean pressure of mercury vapours, kept at a distance of 15 cm from the substrate.

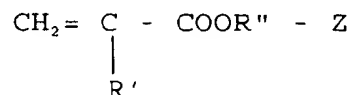
On the film and on the PMMA substrate a temperature near 90°C was reached (polymerization time lower than 5 seconds). The film results opaque and adhesion-free.

Claims

1. Process for preparing shaped articles, plates and films based on acrylic thermoplastic polymers, having antiscratch properties and abrasion-resistant, consisting in applying on the surface of a shaped article based on thermoplastic acrylic

polymers an homogeneous layer of a monomeric composition comprising:

- a) from 40 to 98.5% by weight of at least a (meth)acrylic monomer and/or oligomer having at least two polymerizable double bonds and a boiling temperature higher than the Tg of the acrylic polymers forming the article
- b) from 1 to 20% by weight of at least a polar (meth)acrylic monomer having the following formula



wherein:

R' is H, CH₃; R'' is alkylene C₂-C₆; Z is -OH, -COOH, -SO₃H, -NH₂, -CONH₂ and/or of its oligomers consisting of 2 to 7 monomeric units

c) from 0.5 to 10% by weight of a polymerization initiator at UV light

d) from 0 to 3% by weight of colloidal silica and/or colloidal metal oxides

e) from 0 to 8% by weight of UV stabilizers

f) from 0 to 3% by weight of non ionic surfactants, the sum of the amounts a+b+c+d+e+f being 100, and in submitting the article so coated to UV radiation at temperatures from 20° to 65°C.

2. Process according to claim 1, wherein the thermoplastic acrylic polymers are (co)polymers of esters of (meth)acrylic acid or their mixtures with polyvinylchloride or polyvinylidene fluoride or acrylic elastomers.
3. Process according to claim 1 wherein the thermoplastic acrylic polymer is polymethylmethacrylate.
4. Process according to claim 1 wherein component a) is at least a polyfunctional (meth)acrylate of glycols, polyols, ethoxylated polyols, aliphatic urethanes and melamine.
5. Process according to claim 4, wherein component a) is selected from the group formed by tripropylenglycoldiacrylate, trimethylolpropane triacrylate, 1,6-hexandiol diacrylate, pentaerythrite triacrylate, triacrylate of ethoxylated trimethylolpropane, aliphatic hexacrylate urethane, unsaturated diacrylmelamine or their mixtures.
6. Process according to claim 1, wherein component b) is selected from the group formed by hydroalkyl(meth)acrylates, carboxyalkyl(meth)ac-

rylates, sulphoalkyl(meth)acrylates, aminoalkyl(meth)acrylates, amino carbonylalkyl(meth)acrylates.

7. Process according to claim 6, wherein component b) is hydroxyethylmethacrylate or carboxyethylacrylate. 5
8. Process according to claim 1, wherein the UV irradiation is carried out at temperatures from 30° to 55°C. 10
9. Process according to claim 8, wherein the temperature is from 30° to 55°C. 15
10. Articles based on thermoplastic acrylic polymers, antiscratch and abrasion-resistant, obtainable by the process according to claims from 1 to 9. 20

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Via Masera, 10
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(71) Applicant: **ATOHAAS HOLDING C.V.
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(54) **Process for the preparation of antiscratch and antiabrasion shaped articles based on acrylic polymers**

(57) The invention refers to a process to render antiscratch and antiabrasion shaped articles based on thermoplastic acrylic polymers consisting in coating the article by a composition comprising

a) 40-98.5% by weight of at least a (meth)acrylic monomer and/or oligomer having at least two polymerizable double bonds;

b) 1-20% by weight of at least a (meth)acrylic monomer and/or oligomer containing polar groups;

c) 0.5-10% by weight of a UV photoinitiator;

optionally colloidal silica, UV stabilizers and non ionic surfactants and by polymerizing and crosslinking in situ said composition by UV light, at temperatures of 20-65°C.

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EUROPEAN SEARCH REPORT

Application Number
EP 95 10 7588

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P,X	EP-A-0 652 249 (ATOHAAS C.V.) 10 May 1995 * claims * * page 2, line 52 - line 57 * * page 3, line 35 - line 40 * ---	1-7,10	C08J7/18 C08J7/04 C09D4/02 //C08L33:04
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 11 January 1996	Examiner Niaounakis, M

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! : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document



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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 91-025254[04] & JP-A-2 294 339 (HITACHI CHEMICAL KK) 5 December 1990 * abstract * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 11 January 1996	Examiner Niaounakis, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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